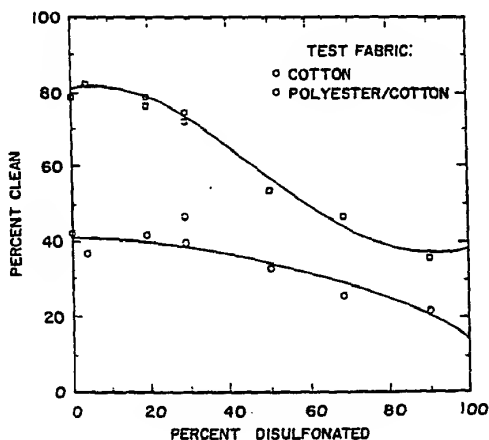




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D 1/83, 3/34, 1/831		A1	(11) International Publication Number: WO 94/05759 (43) International Publication Date: 17 March 1994 (17.03.94)
(21) International Application Number: PCT/US93/08080 (22) International Filing Date: 27 August 1993 (27.08.93) (30) Priority data: 07/936,765 27 August 1992 (27.08.92) US (60) Parent Application or Grant (63) Related by Continuation US 07/936,765 (CIP) Filed on 27 August 1992 (27.08.92) (71) Applicant (for CA only): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : ROSE, Gene, D. [US/US]; 216 East St. Andrews, Midland, MI 48642 (US). COBURN, Charles, E. [US/US]; 3901 McKeith Road, Midland, MI 48642 (US). STRANDBURG, Gary, M. [US/US]; 2256 West Wing Road, Mt. Pleasant, MI 48858 (US). LUTENSKE, Nanette, E. [US/US]; 600 W. Vermont Street, Bay City, MI 48706 (US). KLIER, John [US/US]; 109 Hunters Ridge, Midland, MI 48640 (US). (74) Agent: KANUCH, Bruce, M.; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: CA, US. Published With international search report.	

(54) Title: AN IMPROVED CLEANING COMPOSITION WHICH INCLUDES A SULFONATED ALKYLATED AROMATIC SURFACTANT AND A NONIONIC SURFACTANT



(57) Abstract

This invention is directed to cleaning compositions and methods useful in removing soils, particularly those of oil and grease, from surfaces particularly those of fabric. The composition includes a sulfonated alkylated aromatic surfactant and a non-ionic surfactant. The class of sulfonated alkylated aromatic surfactant analogs used in the cleaning composition of the present invention will comprise at least one benzene ring wherein additional benzene rings can be attached in various forms, for example polycyclic aromatic(s) such as naphthalene, anthracene and the like, or via an ether linkage or other linking atoms. The sulfonated alkylated aromatic (SAA) will include at least one sulfonate group; wherein for aromatics consisting of more than one benzene ring, disulfonate is present in less than 50 percent of the total sulfonated alkylated aromatic. The SAA will also contain at least one alkyl group attached to the aromatic moiety of from about C₁₈ up to about C₃₀.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

-1-

AN IMPROVED CLEANING COMPOSITION
WHICH INCLUDES A SULFONATED ALKYLATED AROMATIC
SURFACTANT AND A NONIONIC SURFACTANT

BACKGROUND OF THE INVENTION

5 This invention is directed to cleaning
compositions and methods useful in removing soils,
particularly those of oil and grease, from surfaces.
The compositions useful in the present invention
contain a sulfonated alkylated aromatic ("SAA")
10 surfactant and a nonionic surfactant.

The largest group of SAA surfactants in use in
cleaning compositions are based on dodecyl benzene
sulfonate; a predominately monoalkylated monosulfonated
15 (MAMS) benzene. Another family of SAA surfactant
analogs are based on diphenyl oxide and are
predominately monoalkylated having a relatively short
(less than C₁₆) alkyl chain and are predominately
disulfonated (MADS DPO). The SAA surfactants of the
20 present invention, on the other hand, are comprised of
at least one longer alkyl side chain (greater than or
equal to C₁₈), are predominantly monosulfonated, and may
contain one or more phenyl groups.

25

-2-

SUMMARY OF THE INVENTION

One aspect of the present invention is an improved cleaning composition which offers superior cleaning of soils especially those of oil and grease. More specifically, the removal of oily particulate stains or soils from surfaces by nonionic surfactants can be substantially improved through the addition of certain sulfonated alkylated aromatic ("SAA") surfactants to the nonionic surfactant.

The class of SAA surfactant analogs used in the cleaning composition of the present invention contain an aromatic moiety comprising at least one benzene ring. The aromatic moiety may contain up to three benzene rings attached in various forms. For example, the aromatic moiety may contain polycyclic aromatic(s) such as naphthalene, anthracene, and the like. Additionally, the aromatic moiety may contain an ether linkage as in diphenyl oxide or biphenylphenyl ether, or other linking atoms. Preferred aromatic moieties are benzene, toluene, xylene, naphthalene, diphenyl oxide, biphenyl, and biphenylphenyl ether.

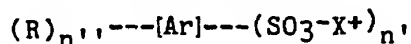
The SAA of the present invention contains at least one alkyl group from a C₁₈ up to about C₃₀. For the purposes of this invention, a monoalkylated SAA refers to a SAA having one alkyl group with a chain length of C₁₈ up to about C₃₀ per aromatic moiety and a dialkylated SAA refers to a SAA having two alkyl groups with chain lengths of C₁₈ up to about C₃₀ per aromatic moiety. Thus, a monoalkylated xylene has one alkyl group of chain length of C₁₈ up to about C₃₀ and two

-3-

methyyl groups. The SAA of the present invention may be monoalkylated or dialkylated.

The SAA of the present invention also includes at least one sulfonate group; wherein for aromatics consisting of more than one benzene ring, disulfonate is present in less than 50 percent of the total SAA. Thus, the aromatic moiety in the present invention is sulfonated to at least about 100 percent and no more than about 150 percent.

The more preferred sulfonated alkylated aromatics are monoalkylated or dialkylated, monosulfonated benzene, toluene, xylene, naphthalene, diphenyl oxide, biphenyl, and biphenylphenyl ether. The SAA of the present invention can be used in its acid or salt/neutralized form. Thus, the SAA surfactant is represented by the following formula:



where:

Ar is an aromatic moiety which may be, but is not limited to, benzene, toluene, xylene, naphthalene, diphenyl oxide, biphenyl, or biphenylphenyl ether;

R is an alkyl group having a chain length of from 18 up to about 30;

X⁺ is hydrogen or a compatible counterion, which may be, but is not limited to NH₄, Na, Ca/2, protonated diethanol amine, or protonated triethanol amine;

$1 \leq n' \leq 1.5$; and

$1 \leq n'' \leq 2$.

The present invention also includes a method of cleaning a stain from a surface of fabric characterized by contacting the stain with the cleaning composition of the present invention comprising a sulfonated alkylated aromatic surfactant and a nonionic surfactant.

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing the influence of the percent of disulfonation of one embodiment of the present invention on pretreatment cleaning.

10

Figure 2 is a graph showing the influence of the percent of dialkylation of one embodiment of the present invention on pretreatment cleaning.

15

Figure 3 is a graph showing the influence of the ratio of the sulfonated alkylated aromatic surfactant to nonionic surfactant in one embodiment of the present invention.

20

Figure 4 is a graph showing the influence of the type of counterion on cleaning performance of one embodiment of the present invention.

25

Figure 5 is a graph showing the influence of water on the cleaning performance of one embodiment of the present invention.

30

Figure 6 is a graph showing the influence of water on the cleaning performance of another embodiment of the present invention.

-5-

DETAILED DESCRIPTION OF THE INVENTION

The sulfonated alkylated aromatic surfactant

Commercially available monophenyl sulfonated alkylated aromatic surfactants useful in the present invention include Aristol F sulfonic acid (available from Pilot Chemical Company), which is a monosulfonated, C₂₀-24 alkyltoluene (monoaromatic) and is greater than 90 percent monoalkylated.

Commercially available alkylated aromatic compounds may be predominantly monosulfonated to be included as SAA surfactants of the present invention. An example of such compounds includes Aristol A synthetic sulfonatable oil available from Pilot Chemical Company. Aristol A is a C₂₀-24 alkylbenzene (monoaromatic) which is at least 80 percent monoalkylated.

The SAA surfactant of the present invention will be monoalkylated or dialkylated and monosulfonated (or no more than 50 mole percent disulfonated for the polyaromatics). The SAA surfactants of the present invention can be prepared by a Friedel-Crafts reaction of an alpha olefin with an aromatic moiety such as diphenyl oxide. The weight percent of the monoalkylated and dialkylated diphenyl oxide (DPO) is determined by gas chromatography of the distilled alkylated diphenyl oxide (ADPO). The alkylates (ADPO) can then be sulfonated with either chlorosulfonic acid or sulfur trioxide and can be used in the acid or salt/neutralized form. The preferred polyaromatic SAA surfactant analog of the present invention has a greater mole percent of monosulfonation relative to disulfonation. The preferred sulfonating agent chosen to produce such an

-6-

analog in a laboratory environment is chlorosulfonic acid. However, a different sulfonating agent, for example sulfur trioxide, may be preferred in a production environment. The percentage of the various sulfonated components (for example disulfonated to unsulfonated, monosulfonated and higher sulfonated) is determined by liquid chromatography.

The Nonionic Surfactant

Nonionic surfactants suitable for inclusion in the present cleaning compositions and methods are chosen to impart compatibility and enhance interfacial interrelations between the cleaning composition, the stain, and the surface from which the stain is to be removed. Suitable nonionic surfactants include, but are not limited to: ethylene oxide adducts of alcohols, alkyl phenols, fatty acids, fatty acid amides and fatty acid esters.

The nonionic surfactant may be monomeric or polymeric. Suitable nonionic surfactants include those taught in the *Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 22, pages 360-377. Preferred surfactants are ethylene oxide adducts of alcohols and alkyl phenols. Preferred nonionic surfactants selected for inclusion in cleaning compositions of the present invention will preferably have a hydrophilic lipophilic balance (HLB) value in the range of from 8 to 15, more preferably 8 to 13, most preferably 9 to 13.

Examples of commercially available nonionic surfactants suitable for the present invention include: Neodol alcohol ethoxylates available from Shell Chemical; Igepal nonylphenol ethoxylates available from

-7-

Rhone Poulenc; and Tergitol nonylphenol ethoxylates available from Union Carbide.

The Cleaning Composition

5 The SAA surfactant and nonionic surfactant ("NS") are typically present in a weight percent of about $5\% \leq \text{SAA}/(\text{SAA} + \text{NS}) \leq 60\%$. The more preferred weight percent for sulfonated alkylated aromatic to nonionic surfactant is about $10\% \leq \text{SAA}/(\text{SAA} + \text{NS}) \leq 50\%$; the most preferred weight percent is about $15\% \leq$
10 $\text{SAA}/(\text{SAA} + \text{NS}) \leq 30\%$. Thus, the weight ratio of sulfonated alkylated aromatic surfactant present to nonionic surfactant present is typically from about 1:19 to about 3:2. Preferably, this weight ratio is from
15 about 1:9 to about 1:1, and more preferably from about 1.5:8.5 to about 3:7.

 The optimal cleaning performance of the composition occurs when the water content of the
20 composition remains below about 30 weight percent of the total composition. Also the addition of hydrocarbon, such as hexadecane, to the formulation in an amount of about 60 weight percent organic solvent (based on the total formulation weight comprised of nonionic
25 surfactant, SAA surfactant and organic solvent) may enhance cleaning performance but the addition of hydrocarbon unpredictably affects the cleaning performance efficacy of the surfactant system.

30 Compositions according to the present invention may take the form of a liquid, emulsion, dispersion or solution, semi-solid or soft solid or stick. Solid stick compositions may be formed by dispersing the various disclosed compositions into a semi-hard carrier medium. An example of a semi-hard carrier medium is

-8-

sodium stearate. Solid stick pre-spotting in stain removing compositions and methods for making and using such a solid stick are described in the U.S. Patents 4,842,762; 4,396,521; and 3,664,962.

5 Methods for cleaning a soil or stain on a surface or fabric are characterized by contacting the soil or stain with any of the cleaning compositions of the present invention described hereinabove. Contacting
10 the soil or stain with the cleaning composition may mean contacting the area of the surface or fabric where the stain or soil resides, in addition to directly upon the stain itself. The term "stain" includes any substance which is embedded or not embedded, solid or liquid, wet
15 or dry, and at or beneath the surface or fabric.

 After any of the cleaning compositions of the present invention have been applied to, or contacted with the stain, the stain may be removed by wiping with
20 a substrate, such as a wet cloth or sponge; or by contacting the stain with water, such as by washing with a substantially aqueous media. In the case of fabric the composition treated stain is preferably laundered with water and more preferably with an aqueous solution
25 of mostly water and a conventional laundry detergent.

 The cleaning formulations of the present invention are evaluated by measuring the efficacy of the formulation as a prewash stain remover treatment for
30 soiled fabric. The cleaning formulation is applied to prestained fabric and the fabric is washed and evaluated for cleaning efficacy by a reflectance measurement of the washed fabric compared to that of the unstained fabric and the stained fabric.

-9-

The following examples illustrate (1) the preparation of the SAA surfactants of the present invention; (2) the performance of these surfactants with nonionic surfactants as a cleaning composition and (3) the performance of commercially available SAA surfactants with nonionic surfactants as components of the cleaning composition.

Examples

10 The Sulfonated Alkylated Aromatic Surfactants

I. PREPARATION OF DIPHENYL OXIDE OR BIPHENYL SULFONATED ALKYLATED AROMATIC SURFACTANTS (SAA).

Alkylates prepared (percentages are by weight):

- 15 * C₆ monoalkylated diphenyl oxide (DPO)
(comparative example - not an example of the invention)
- * C₁₄ dialkylated DPO (comparative example - not an example of the invention)
- 20 * C₁₆ monoalkylated DPO (comparative example - not an example of the invention)
- * C₁₈ dialkylated DPO
- * C₂₀₋₂₄ monoalkylated DPO
- 25 * C₂₀₋₂₄ 75%/25% mono/di alkylated DPO
- * C₂₄₋₂₈ 80%/20% mono/di alkylated DPO
- * C₃₀₊ 80%/20% mono/di alkylated DPO
- * C₂₀₋₂₄ 80%/20% mono/di alkylated biphenyl (BP)

30 (All of the alpha olefins used to prepare the above alkylates were obtained from Chevron Corporation, therefore, the chain length specifications are those furnished by Chevron.)

-10-

General procedure to prepare alkylated aromatic compounds:

Preparation of C20-24 monoalkylated diphenyl oxide (DPO): Into a 5 liter round-bottomed flask (RBF) equipped with a magnetic stirrer, an addition funnel, a condenser, and a nitrogen inlet is placed warm DPO, (2.040 kg, 12.00 moles, 3 mole equivalents with respect to the olefin). To this light yellow solution is added the Lewis acid catalyst, aluminum chloride, AlCl_3 , (24.0 g, 0.180 moles, 0.045 mole equivalents with respect to the olefin). This is then heated to 70-75 °C with stirring for 45 minutes so as to completely dissolve the AlCl_3 . The color of the reaction mixture will gradually darken during this time until it is red brown. Concurrently, the C20-24 alpha olefin (1.185 kg, 4.00 moles) is melted and placed into an addition funnel that has been wrapped with heating tape. The addition of the olefin is begun once all of the AlCl_3 dissolves into the DPO. The rate of olefin addition is to maintain the temperature at 70-75 °C (over about 5 hours).

Once all of the olefin is added, external heating is reapplied and the reaction mixture is post reacted at 70 °C for an additional hour. At the end of the hour, heating is discontinued and a 25% aqueous sodium hydroxide solution (349 g) is introduced. The reaction mixture is allowed to cool and stir overnight during which time the color changes from a rather dark red brown to a light yellow.

The stirring is discontinued and the phases are allowed to separate. The organic phase is decanted away from the basic aqueous phase, is placed into several 2 liter separatory funnels and is washed several times with distilled water until the pH of the resulting water

-11-

is neutral. The organic phases are then combined and stored in plastic containers until needed.

General procedure for topping alkylated aromatic compounds, simple distillation:

5 The removal of the unreacted DPO (diphenyl
oxide) (ca. 1.3 kg, 2.0 mole equivalents) is
accomplished through the use of a simple vacuum
distillation. The washed organic phase portion from
above (ca 3.5 liters) is placed into a 5 liter RBF
10 equipped with a magnetic stirrer, a simple distillation
head apparatus and a vacuum take off adapter. The
reaction mixture is stirred and the vacuum is slowly
applied in order to minimize bumping. The distillation
proceeds as follows (Table 1):
15

20

25

30

-12-

Table 1: Simple distillation to top C20-24 ADPO.

FRACTION NUMBER	BOILING POINT RANGE (°C/Torr)	AMOUNT OBTAINED	VISUAL APPEARANCE	WEIGHT PERCENT COMPOSITION			
				DPO	OLEFIN	MONO ADPO	DI ADPO
1	<60/0.2	600 g	clear, colorless	100	N/D	N/D	N/D
2	75/0.7 - 60/0.2	800 g	clear, colorless	100	N/D	N/D	N/D
3	60/0.2	450 g	clear, colorless	99	1	N/D	N/D
4	60/0.2 - 130/0.12	NIL	clear, colorless	N/A	N/A	N/A	N/A
5	130/0.12 - 206/0.15	4 g	lt. yellow	99	1	N/D	N/D
6	206/0.12 - 209/0.12	14 g	lt. yellow	N/D	47	54	N/D
7	209/0.12 - 212/0.12	16 g	lt. yellow	N/D	3	97	N/D
8	212/0.12	38g	lt. yellow	N/D	0.1	99.9	N/D
POT	>212/0.12	1800g	lt. yellow	N/D	0.7	75	25

N/A =not available, N/D = not detected

-13-

The pot material is then used as the topped material in subsequent sulfonation reactions or alternatively could be fractionally distilled to obtain fractions that contain varying degrees of alkylated materials (i.e. mono/di/higher alkylate).

5

General procedure for the isolation of mono/di/higher alkylated aromatic compounds using a vacuum fractional distillation:

10 Topped material (0.9 liters) is placed into a 2 liter RBF equipped with a magnetic stirrer, a 14 inch vigreux fractionating column and a vacuum distillation head. The contents are stirred and the vacuum is applied. The distillation proceeds as follows (Table 2):

15

20

25

30

-14-

Table 2: Fractional distillation to separate alkylated components based on the number of alkyl chains (example C20-24 ADPO).

FRACTION NUMBER	BOILING POINT RANGE (°C/Torr)	AMOUNT OBTAINED (grams)	VISUAL APPEARANCE	WEIGHT PERCENT COMPOSITION			
				DPO	OLEFIN	MONO ADPO	DI ADPO
1	212/0.12	38	light yellow	N/D	0.1	99.9	N/D
2	212/0.12	150	light yellow	N/D	N/D	100	N/D
3	212/0.12 - 214/0.12	245	light yellow	N/D	N/D	100	N/D
4	214/0.12 - 220/0.12	110	light yellow	N/D	N/D	99.9	N/A
5	220/0.12 - 224/0.15	55	light yellow	N/D	0.2	99.7	0.1
6	224/0.15 - 230/0.25	35	light yellow	N/D	0.9	97.4	1.7
7	230/0.25 - 242/0.4	30	dark yellow	N/D	2.2	91.7	6.2
8	242/0.4 - 275/1.0	30	dark yellow	N/D	7.1	53.5	39.4
POT	> 275/1.0	185	brown	N/D	N/D	N/D	100

-15-

The pot material is used as dialkylated DPO based material in subsequent sulfonation reactions and in the GC standard solution.

Sulfonates prepared:

- 5 * C₆ monoalkylated monosulfonated DPO (comparative example - not an example of the invention)
- * C₁₄ dialkylated, monosulfonated DPO (comparative example - not an example of the invention)
- 10 * C₁₆ monoalkylated, monosulfonated DPO (comparative example - not an example of the invention)
- * C₁₈ monoalkylated, monosulfonated DPO
- * C₁₈ dialkylated, monosulfonated DPO
- 15 * C₂₀₋₂₄ topped material, monosulfonated DPO
- * C₂₀₋₂₄ monoalkylated, disulfonated DPO (comparative example - not an example of the invention)
- * C₂₀₋₂₄ monoalkylated, monosulfonated DPO
- 20 * C₂₄₋₂₈ topped material, monosulfonated DPO
- * C₃₀₊ topped material, monosulfonated DPO
- * C₂₀₋₂₄ topped material, monosulfonated BP

25 General procedure for the monosulfonation of aromatic materials:

 C₂₀₋₂₄ monosulfonated monoalkylated DPO: Into a 1 liter RBF equipped with a magnetic stirrer, additional funnel, Claisen adapter, water condenser, 30 nitrogen inlet and a hydrochloric acid exit is placed the C₂₀₋₂₄ monoalkylated DPO (175.0 g, 0.380 moles). This is diluted with chloroform (350 mL) and cooled to 0°C via an ice bath. To the addition funnel is added chloroform (50 mL) and chlorosulfonic acid (25.3 mL, 0.380 moles). The contents of the addition funnel are

-16-

5 mixed and added into the reaction vessel over a 2 h period. During this time the reaction mixture's color goes from nearly colorless to red-brown. Once all the the chlorosulfonic acid solution is added, the reaction mixture is allowed to slowly warm to ambient temperature and stir overnight. The following day an aliquot is removed and analyzed by liquid chromatography to determine the degree of sulfonation. When it is apparent that the reaction is complete, the stir bar is removed and the contents are concentrated in vacuo (5-10 10 torr) utilizing a rotary evaporator. The sample is then subjected to reduced pressures (0.1-0.5 torr, vacuum pump) and a final sample is analyzed by liquid chromatography. Both liquid chromatography analyses are 15 consistent and show that the percent of unsulfonated and monosulfonated product to the disulfonated material is about 96 to 4.

20 General procedure for the purification of monoalkylated, monosulfonated aromatic materials (example C20-24 DPO based MAMS):

C20-24 DPO based MAMS: A portion of the crude reaction mixture described above is taken (70 g) and dissolved in methylene chloride, MeCl_2 , (300 mL) and 25 placed on top of a flash silica gel column (10 inch x 2 inch) that has been packed using MeCl_2 . Some solid material may fail to dissolve into the MeCl_2 , and is assumed to be inorganic salts such as sodium sulfate and sodium chloride. The elution method and the subsequent 30 analysis (TLC, elution with MeCl_2 ; or liquid chromatography) of the fractions obtained are shown in Table 3.

-17-

Table 3: Column chromatography results of C20-24 monosulfonated, monoalkylated DPO based material (MAMS).

FRACTION NUMBER	SOLVENT SYSTEM	AMOUNT OF ELUENT	AMOUNT OF MATERIAL	VISUAL APPEARANCE	MATERIAL ANALYSIS
1	MeCl ₂	300	NIL	N/A	N/A
2	HEXANE (H)	500	13.6	LIGHT YELLOW	ALKYLATE
3	H	500	NIL	N/A	N/A
4	40% MeCl ₂ /H	400	0.2	CLEAR	ALKYLATE
5	40% MeCl ₂ /H	400	0.8	CLEAR	ALKYLATE
6	1:1 MeCl ₂ /H	500	NIL	N/A	N/A
7	MeCl ₂	800	0.1	N/A	ALKYLATE
8	1% MeOH/MeCl ₂	800	1.5	PALE YELLOW	MAMS
9	2% MeOH/MeCl ₂	800	32.5	DARK YELLOW	MAMS
10	5% MeOH/MeCl ₂	500	9.0	YELLOW	MAMS
11	5% MeOH/MeCl ₂	500	6.0	PALE YELLOW	MAMS
12	MeOH	500	5.0	CREAM COLOR	70% MAMS/30% MADS

-18-

The column chromatograph is discontinued when the MADS component is detected eluding from the column. Fractions are combined based upon their purity. Fractions 1 through 7 contain unreacted alkylate and are discarded. Fraction 8 through 11 contain only pure C20-24 MAMS and are combined to afford 45 g of product.

General procedure for the disulfonation reaction of aromatic materials:

C20-24 disulfonated monoalkylated DPO: To a 125 mL addition funnel is added liquefied sulfur trioxide, SO₃, (56.6 g, 0.707 moles, 2.3 equivalents based on ADPO (alkylated diphenyl oxide)). This is sealed and transferred to a bottom outlet, stopcock controlled, 500 mL 3-necked RBF that is equipped with a stir rod, a nitrogen inlet and contains MeCl₂ (150 mL). The amount of the C20-24 monoalkylated DPO (143.6 g, 0.308 moles, 1/2.3 equivalents) is calculated based on the amount of the SO₃ weighed out and is placed into a 1 liter 3-necked RBF equipped with a nitrogen inlet and overhead stirrer. The alkylate is diluted with MeCl₂ (350 mL) and the 1 liter 3-necked RBF is attached to the outlet of the SO₃/MeCl₂ RBF. The reaction vessel is cooled to 0 °C via an ice bath. The alkylated DPO solution is stirred and the SO₃/MeCl₂ solution is slowly added over 1.5 h being careful not to allow the reaction temperature to rise above 4 °C. During this time, the reaction darkens from light yellow to red brown. An aliquot is removed after a post reaction time of 0.5 hours at 0 °C and is concentrated, neutralized and dissolved in a water/methanol mixture. This is analyzed by liquid chromatography. This analysis indicated that the ratio of unsulfonated/monosulfonated ADPO to disulfonated ADPO is about 2 to 98.

-19-

For the cleaning formulations of the present invention the purity of the monoalkylated, disulfonated DPO based species are generally pure enough that no further purification techniques are required.

5 General procedure for the analysis of the alkylates:

 The analysis of the alkylates is done using a gas chromatography system comprised of a Hewlett Packard GC; HP 7673 A autosampler; HP3396A integrator; HP 9114B
10 external disk drive and a J&W DB, 15m x 0.32 mm, 0.1 um film column. The flow rate of helium is 8.7 ml/min. The instrument is calibrated with an internal standard and a standard solution of components. The percentages reported are in weight percent. Each different ADPO
15 (differing by chain length) prepared required development of a separate GC system.

 General procedure for the analysis of the sulfonated aromatic species:

20 The analysis of the sulfonated aromatic species is done using a liquid chromatography system comprised of a Milton Roy piston pump, a single port injector, a 250 mm x 4.6 mm glass column packed with Vydac's 301SC (200 mm) anion exchange resin, a LDC UV III monitor (254
25 nm filter), and a Spectra Physics Chrom Jet integrator. The solvent system is a 1:1 methanol (MeOH):tetrahydrofuran (THF); buffered with 0.2 M acetic acid (AcOH), 0.2 M sodium acetate (NaOAc), and 0.1 M
30 sodium perchlorate (NaClO₄). The operating pressure is kept between 50-80 psi with dampening. The percentages reported are in area percent.

-20-

II. PREPARATION OF CLEANING COMPOSITION/ STAINED FABRICS/EVALUATION OF CLEANING

Preparation of cleaning composition

5 The cleaning samples prepared all contained alkylated, sulfonated aromatic materials and nonionic surfactants in various ratios according to the figures and tables which follow in the results section. The alkylated, sulfonated aromatic component is the formula as stipulated in the figures and tables which follow.

10 The nonionic surfactant component of the cleaning formulation is either Neodol alcohol ethoxylates available from Shell Chemical; Igepal nonylphenol ethoxylates available from Rhone Poulenc; Tergitol
15 nonylphenol ethoxylates available from Union Carbide or one of three blends prepared from Neodol to impart various HLB surfactant solutions. Blend one (HLB value approximately 9) consists of approximately 77 weight percent Neodol 25-3 and approximately 23 weight percent
20 Neodol 25-9; blend two (HLB value approximately 10) consists of approximately 50 weight percent Neodol 23-3 and approximately 50 weight percent Neodol 23-6.5 ; blend three (HLB value approximately 11.4) consists of
25 approximately 32 weight percent Neodol 25-3 and approximately 68 weight percent Neodol 25-9.

Preparation of fabric

Test fabrics are:

- 30
- 1) Cotton: #405, Bleached Cotton Sheeting, 48" wide, obtained from Test Fabric Incorporated, Middlesex, NJ
 - 2) Polyester/Cotton: #7436, Dacron 54W/Cotton, 65/35, Poplin, 60" wide,

-21-

obtained from Test Fabric Incorporated,
Middlesex, NJ

The fabric is prewashed three times to remove
sizing in a General Electric Washer Model #WWA8340G.

5 Settings used for all cycles are as follows:

Regular/Normal cycle

Warm wash/cold rinse

Load size: large

10 Generally, one piece of cotton fabric, 45" x 96", and
one piece of polycotton fabric, 60" x 72", are laundered
per wash load. Zero phosphorous content TIDE® powdered
laundry detergent (Proctor & Gamble) is used for this
prewash and in all phases of testing. For each wash

15 cycle, 15± 0.5 grams of TIDE is used. The fabric is not
dried between wash cycles. After the third wash cycle,
the fabric is dried in a General Electric Dryer Model
#DDE8200GBLAD on high heat for 70 minutes. After

20 drying, the fabric is referred to as prewashed fabric.
The fabric is removed promptly from the dryer and
smoothed with clean hands to remove wrinkles. The
prewashed fabric is not ironed. If it is not used in a
test within six weeks it is discarded.

25 Cutting swatches

After drying, the prewashed fabric is cut into
swatches approximately 3" x 4.5". An Eastman Chick-a-
dee Model D2 rotary shear (MJ Feley Company, Roseville,
30 MI) is used for the cutting procedure. Metal templates
of cleaned aluminum or cleaned galvanized sheeting are
used as guides for the rotary shear. Fabric salvages
are permissible on the final test swatch. Once cut into
the 3" x 4.5" test size the prewashed fabric is referred

-22-

to as a swatch or a test swatch. All swatches are stored away from light.

Staining of swatches

5 Staining of swatches is done in the afternoon of the day before a cleaning test. A 24 hours set time between staining and testing is recommended to allow the stain to wick out across the swatch. The swatches to be stained are laid out on a bench top on a double
10 thickness of Scott Utility Wipes (referred to as Scott wipes). All swatches should be from the same prewashed fabric.

Number of swatches to stain: Generally for
15 each cleaning formulation tested two stained cotton swatches and two stained polycotton swatches are treated and washed with TIDE and two stained cotton swatches and two stained polycotton swatches are treated and washed
20 without TIDE. Controls are two stained cotton swatches and two stained polycotton swatches washed in TIDE only. Also, three stained swatches of each fabric type are needed as 100% Dirty Standards.

Stain material: The stain material is Wolf's
25 Head® SAE 30W motor oil (Wolf's Head Oil Company, Oil City, PA) used approximately 30 hours in an International three cylinder diesel tractor. Since the stain contains particulates, the stock bottle is shaken
30 at high speed on a reciprocation shaker for five minutes before it is applied. If the staining process takes longer than 15 minutes, the stock bottle will be reshaken after 15 minutes.

Applying the stain: The stain can be applied in one of three ways. All three methods result in

-23-

approximately 0.18 grams of stain material being applied. Method 2 or 3 is recommended.

- 5 1) Plastic disposable pipet (Fisher Scientific Company, Fisherbrand Catalog #13-711-5).
Fill pipet and hold it at 45° angle about one inch above the center of the swatch. Slowly drip on seven drops at the center of each swatch.
- 10 2) Nichiryo Oxford model 8100 syringe pipet
(Fisher Scientific Company) with a 6 milli liter syringe on the end. Dispenser setting at 2 to give 200 microliters (\pm 0.8% accuracy as manufactured) volume
15 dispensed. Slowly dispense the stain material at the center of the swatch with the tip of the syringe about one inch above it.
- 20 3) Weighed amount. Tare out the swatch on a Scott Wipe on a two decimal place balance and apply $0.18\text{g} \pm 0.02$ of stain material
25 slowly by pipet to the center of the swatch.

25 After staining: After applying the oil stain, the swatches sit undisturbed overnight on a bench top. The swatches are now referred to as stained swatches.

- 30 Stained swatches will sit a minimum of 16 hours after staining before being used in a test. This is to allow the stain to 'set'/wick out into the swatch. Stained swatches not used within 28 hours of staining are discarded.

-24-

Preparation of stained swatches for testing

Stained swatches are inspected before testing. Any that look unusual, i.e. the oil stain did not spread out or only spread unevenly, are discarded. Extra
5 stained swatches will not be held over to be used in another cleaning test.

Two cotton and two polycotton stained swatches are laid out on a new clean Scott wipe. If possible,
10 the technical cleaning formulation is stirred with a wooden applicator stick. A stained swatch is tared. The stained swatch is removed to a Scott wipe and approximately 1.5 grams of the technical cleaning
15 formulation is applied. A wooden applicator stick is used to gently spread it over the surface of the stained area. A rubbing motion is not used. High viscosity technical cleaning formulation may require more sample
20 and more work to spread them. Low viscosity technical cleaning formulations may be transferred to the stained swatch by volumetric syringe.

The technical cleaning formulations is spread to cover a diameter of 1.5 inches at the center of the
25 stained area and at least 90% of the full stained area. The treated stained swatch is placed on the balance and the amount of technical cleaning formulation applied recorded. The amount applied should be 1.5 ± 0.2 g. The balance pan is cleaned and the next stained swatch
30 in the set of four is processed in the same way. Once the technical cleaning formulation is applied, the stained swatch is referred to as a treated stained swatch.

-25-

In order to keep the contact time between stain and technical cleaning formulation in the selected range of a minimum of 5 minutes and a maximum of 30 minutes, no more than 25 minutes should lapse between the first swatch and the last swatch in the set is treated.

5 Ideally, no more than ten minutes should lapse before all stained swatches in the set are treated. Five minutes after the last stained swatch in the set is treated, the treated stained swatches are put into a prepared agitator pot of a Terg-O-Tometer (SEE

10 PREPARATION OF TERG-O-TOMETER SECTION). The treated stained swatches are introduced into the wash water in the order in which they were treated.

15 The above process is generally done twice for each technical cleaning formulation with one set washed in water with TIDE present and the second set washed in water without TIDE present. Stained swatches treated with different technical cleaning formulations are not

20 washed together.

Preparation of controls

For each test day, controls are run with TIDE

25 only. Two cotton stained swatches and two polycotton stained swatches are introduced into an agitator pot prepared with 2.00 ± 0.01 g TIDE in the water. Controls are processed the same as technical cleaning formulation treated stained swatches.

30

Preparation of terg-o-tometer and testing with terg-o-tometer

Deionized water is used in all phases of testing after the initial prewash of the fabric.

-26-

A six place Terg-O-Tometer model #7243S (Research and Testing Company, Inc. Fairfield, NJ) is used. The Terg-O-Tometer bath is preheated to 120°F. The agitator pots are filled with 1700 \pm 50 mL of deionized water. The wash and rinse cycles are run at 120°F and the agitation rate is 100 rpm. The temperature is checked in each agitator pot.

Wash cycle

Unless specified otherwise, stained swatches are washed with TIDE in the water: 0.5 grams of TIDE is used for each swatch. Generally four swatches are washed in 2 \pm 0.01 grams of TIDE per agitator pot. The lot code of the TIDE box is recorded. TIDE is added to the agitator pot, with agitation on, for approximately two minutes before the swatches are added.

For stained swatches with or without TIDE in the water: treated stained swatches are added one at a time to the agitator pot, with agitation on, in the order in which they were treated with the treated side facing away from the agitator shaft. After all the swatches are added to a pot, a timer is set for 15 minutes. At the end of 15 minutes, agitation is stopped. The contents of the agitator pot are poured through a sieve, retaining the washed treated stained swatches (washed swatches). The washed swatches are retrieved and the excess water squeezed out of them by hand. They are rinsed for 3-5 seconds with deionized water. The washed swatches are then separated from each other.

-27-

Rinse cycle

The rinse cycle is the same for all swatches whether washed with or without TIDE.

5 The separated washed swatches are immediately added one at a time to a rinse agitator pot. A rinse agitator pot contains 1700 ± 50 mL deionized water at 120°F. There is no specific order of addition for a
10 rinse cycle. Agitation and water temperature is the same as for a wash cycle. A rinse cycle is five minutes in length. At the end of the five minutes, the contents of the rinse agitator pot is poured through a sieve, retaining the washed and rinsed swatches (rinsed
15 swatches). Rinsed swatches are separated by hand and rinsed 3-5 seconds with deionized water. Excess water is squeezed out of the rinsed swatches by hand. The rinsed swatches of each set are smoothed flat by hand onto a single thickness of Scott wipe. A second Scott
20 wipe is used to lightly cover the rinsed swatches. The rinsed swatches are not ironed and are allowed to dry overnight.

Determination of percent clean

25 Percent clean is calculated from reflected light readings. Reflectance readings are reported as three coordinates that define a specific point in the cubic space that is used to described color and hue.
30 Reflected light readings from a set of 100% Clean Standards and from a set of 100% Dirty Standards are used to determine the range for zero to 100% clean. The reflectance of a rinsed swatch is then placed as a percentage along this range and this percentage is reported as its percent clean.

-28-

Rinsed swatches are air dried at least overnight (16 hours) before reflectance readings are taken. Rinsed swatches not read within 24 hours of test will be stored in a dark place to prevent deterioration. A MiniScan™ Spectrocolorimeter version MS4500L (Hunter Lab, Reston VA) is used to make reflectance measurements and is standardized before each reading session. The Commission Internationale de l'Eclairage (CIE) 1931 Tristimulus XYZ Scale (CIE XYZ Scale) is used as the reflectance scale with a CIE 1931 standard source illuminant C and CIE 1931 2° standard observer.

At least two readings for each rinsed swatch is done with the sensor of the MiniScan rotated 90° to minimize the effect of fabric nap on the reflectance readings. The average of these readings is recorded. Readings are taken at the center of a rinsed swatch on the side to which the technical cleaning formulation is applied. The rinsed swatch is laid on a piece of white poster board to give a uniform background to all rinsed swatches and to eliminate the tendency of the rinsed swatch to pillow up. Pillowing up would occur on a soft background and effect the reflectance angle of the light and therefore the reflectance reading.

Standards will consist of three unstained swatches of each fabric (100% Clean Standards) from the same prewashed cloth as the test set and three stained swatches of each fabric (100% Dirty Standard) from the same staining day as the test set and from the same prewashed cloth. Readings are done using the same method as for the rinsed swatches.

-29-

Determination of percent clean is by the following equation:

(1) Percent Clean =

5
$$100 * \{ [(X_r - X_d)^2 + (Y_r - Y_d)^2 + (Z_r - Z_d)^2]^{1/2} / [(X_c - X_d)^2 + (Y_c - Y_d)^2 + (Z_c - Z_d)^2]^{1/2} \}$$

Where:

10 X_c = clean standard swatch X value from MiniScan
 Y_c = clean standard swatch Y value from MiniScan
 Z_c = clean standard swatch Z value from MiniScan

X_d = dirty standard stained swatch X value from MiniScan

15 Y_d = dirty standard stained swatch Y value from MiniScan

Z_d = dirty standard stained swatch Z value from MiniScan

X_r = Rinsed swatch X value for MiniScan

20 Y_r = Rinsed swatch Y value for MiniScan

Z_r = Rinsed swatch Z value for MiniScan

25

30

-30-

III. EVALUATION OF SAMPLES/CLEANING FORMULATION

Cleaning formulations to be tested are prepared by combining the desired amount of a sulfonated alkylated aromatic surfactant, nonionic surfactant and any additional additives to be included in the formulation and mixing them until uniform. The formulations may require heating to facilitate mixing.

10 Formulation Variables

A. Type of Sulfonated Alkylated Aromatic Surfactant

1) Alkyl chain length

15 Table 4 summarizes the cleaning results for a series of substantially monoalkylated monosulfonated diphenyl oxide (MAMS DPO) surfactants and various alkylbenzene sulfonic acids when used in a formulation consisting of 1 part of the sulfonated alkylated aromatic surfactant to 3 parts of Igepal CO-520 nonionic surfactant. Data with TIDE detergent without any stain pretreatment are included in the table for comparison.

25 A comparison of the data show that the percent cleaning obtained with a sulfonated alkylated aromatic surfactant containing an alkyl group of C₁₈ or longer are considerably superior to the cleaning obtained with the Comparative Examples or a typical detergent (TIDE).
30 The MAMS DPO demonstrates the most dramatic improvement in cleaning performance from the C₁₆ to C₁₈ alkyl chain length.

-31-

Table 4

The Influence of Alkyl Chain Length on Cleaning Performance

5	Sulfonated Surfactant	mono/ di- alkylate (weight percent)	mono/ di- sulfonate (area percent)	Percent Clean (washed in Tide)		Percent Clean (Not washed in Tide)	
				Cotton	Polyester/ cotton	Cotton	Polyester/ cotton
10	C ₆ MAMS DPO Comparative Example A	100/0	84/16	36	29		
	C ₁₆ MAMS DPO Comparative Example B	100/0	93/7	38	33	44	24
15	C ₁₈ MAMS DPO	100/0	97/3	60 ¹	40 ¹	57	26
	C ₂₀₋₂₄ MAMS DPO	74/26	86/14	75 ²	46 ²	81	35
	C ₃₀ + MAMS DPO	80/20	85/15	70	58		
20	p-Toluene sulfonic acid Comparative Example C			33	12	5	7
	C ₁₂ Benzene sulfonic acid ³ Comparative Example D			34	27	37	23
25	C ₁₈ Toluene sulfonic acid ⁴	97/3	100/0	42	31		
	C ₂₀₋₂₄ Toluene sulfonic acid ⁵	93/7	100/0	77 ²	47 ²	76	30
30	Tide alone Control - not an example of the invention			24 ⁶	11 ⁶		

1. Average of 2 tests.

2. Average of 6 tests.

3. BIO SOFT S-100[®], Stepan

4. Aristol G, Pilot Chemical

5. Aristol F, Pilot Chemical

6. Average of 20 tests.

-32-

Table 4
The Influence of Alkyl Chain Length on Cleaning Performance

Sulfonated Surfactant	mono/ di- alkylate (weight percent)	mono/ di- sulfonate (area percent)	Percent Clean (washed in Tide)		Percent Clean (Not washed in Tide)	
			Cotton	Polyester/ cotton	Cotton	Polyester/ cotton
Igepal CO-520 alone Control - not an example of the invention			25	23		

1. Average of 2 tests.
2. Average of 6 tests.
3. BIO SOFT S-100®, Stepan
4. Aristol G, Pilot Chemical
5. Aristol F, Pilot Chemical
6. Average of 20 tests.

In all cases the data show that cleaning with formulations containing the sulfonated alkylated aromatic surfactant containing an alkyl group of 18 carbons or longer gave better performance than the nonionic surfactant by itself or the nonionic surfactant containing a commonly available linear dodecylbenzene sulfonic acid (BIO SOFT S-100® from Stepan Chemical Co. Northfield IL.) or a commonly available hydrotrope (p-toluene sulfonic acid).

2) Percent of sulfonation

The percent of sulfonation is evaluated by preparing cleaning formulations of Igepal CO-520 with SAA surfactants containing different ratios of mono- to disulfonated C₂₀₋₂₄ alkylate diphenyl oxide that have been separately prepared using the same batch of C₂₀₋₂₄ monoalkylated diphenyl oxide. The predominantly monosulfonated DPO is analyzed to be 100 percent monoalkylated, 96 percent monosulfonated, and 4 percent

-33-

disulfonated; the predominantly disulfonated DPO is analyzed to be 100 percent monoalkylated and 90 percent disulfonated. A purified monosulfonated, monoalkylated DPO is prepared and analyzed to be 100 percent monoalkylated and 100 percent monosulfonated.

5

Figure 1 summarizes the influence of the percent of sulfonation on the cleaning for a formulation consisting of 1 part of the mono- and disulfonated C20-24 monoalkylate diphenyl oxide surfactant to 3 parts by weight of Igepal CO-520 nonionic surfactant. The cleaning performance begins to decrease after about 30 percent by weight of the C20-24 monoalkylated diphenyl oxide is disulfonated.

10

PERCENT CLEAN DATA FOR FIGURE 1

	<u>% Monosulfonated</u>	<u>% Clean Cot</u>	<u>% Clean PEC</u>	<u>% Disulfonated</u>
	10.0	36	22	90.0
	31.5	47	26	68.5
20	50.0	54	33	50.0
	71.3	75	40	28.7
	71.3	73	47	28.7
	80.8	79	42	19.2
25	80.8	77	42	19.2
	96.0	82	37	4.0
	100.0	79	42	0.0

30

3) Percent of alkylation

The percent of alkylation is evaluated by preparing formulations with different ratios of mono- to dialkylated C18 alkylated diphenyl oxide (DPO). The monoalkylated DPO is analyzed to be 99.9% monoalkylated and 97% monosulfonated; the dialkylated DPO is analyzed

-34-

to be 100% dialkylated and 84% monosulfonated. Figure 2 summarizes the percent of alkylation influence on the cleaning for a formulation consisting of 1 part of the mixture of the sulfonated mono- and dialkylated C₁₈ diphenyl oxide surfactant to 3 parts of Igepal CO-520 nonionic surfactant; for polyester/cotton fabric the cleaning performance is essentially independent of the ratio of the degree of alkylation. However, for cotton fabric, significantly better cleaning performance is obtained with the dialkylated surfactant than with the monoalkylated surfactant. Also, a minimum in the cleaning performance is observed at approximately 30 weight percent of dialkylation.

The influence of increased chain length on cleaning performance for monosulfonated dialkylated aromatic surfactants is shown in Table 5 for both diphenyl oxide and benzene based surfactants. This table illustrates three trends, firstly, the data demonstrate that cotton cleaning performance is enhanced by increasing the length of the alkyl group for both diphenyl oxide and benzene based surfactants. Secondly, superiority of the cleaning is observed with the sodium salt of C₁₆ dialkylated DPO compared to the sodium salt or acid form of the C₁₆ monoalkylated DPO and the dodecylbenzene sulfonic acid. Finally, a comparison of Table 4 with Table 5 shows cleaning performance enhancement is preferably obtained with a monosulfonated long chain monoalkylated aromatic surfactant than by a similar equivalent weight monosulfonated dialkylated aromatic surfactant in which its two shorter alkyl chains are roughly one half the length of the long chain used to prepare the monosulfonated monoalkylated aromatic surfactant.

-35-

PERCENT CLEAN DATA FOR FIGURE 2

	<u>% Monoalkylation</u>	<u>% Dialkylation</u>	<u>% Clean Cot</u>	<u>% Clean PEC</u>
	100.0	0.0	59	39
	100.0	0.0	62	40
5	100.0	0.0	63	33
	100.0	0.0	60	32
	94.4	5.6	57	38
	94.4	5.6	61	32
10	89.9	10.1	54	38
	89.9	10.1	55	36
	80.8	19.2	54	35
	80.8	19.2	48	33
15	70.2	29.8	50	33
	70.2	29.8	48	39
	50.1	49.9	57	39
	50.1	49.9	60	34
20	40.0	60.0	59	32
	25.0	75.0	66	33
	10.0	90.0	75	31
	0.0	100.0	77	41
25	0.0	100.0	73	34

4) Type of Aromatic Moiety

The influence of the type of aromatic moiety on cleaning performance is illustrated in Table 3A for C18 and C20-24 alkyl chain lengths used in formulations consisting of 1 part by weight of the monosulfonated monoalkylated aromatic surfactant to 3 parts by weight of Igepal CO-520 nonionic surfactant. These data show that with the C20-24 alkyl chain length, the type of aromatic moiety has little effect on the type of

-36-

Table 5
The Influence of Dialkyl Chain Length on Cleaning Performance

Sulfonated Surfactant	mono/di-alkylate (weight percent)	mono/di-sulfonate (area percent)	Percent Clean	
			Cotton	Polyester/ cotton
C ₁₈ DAMS DPO ¹	0/100	84/16	75 ⁶	38 ⁶
C ₁₄ DAMS DPO ¹ (comparative example)	0/100	92/8	54	24
C ₁₀ DAMS DPO ¹ (comparative example)	0/97 ⁷	94/6	37	27
C ₁₂ DA BSA ^{2,3} (comparative example)	>90% dialkylate	100/0	71 ⁶	26 ⁶
C ₁₀ DA BSA ² (comparative example)	100/0	100/0	32	28
C ₁₆ MAMS DPO ⁴ (comparative example)	100/0	93/7	38	33
C ₁₆ MAMS DPO ⁴ Na salt (comparative example)	99.8/0.2	91/9	30	38
C ₁₆ DAMS DPO ⁴ Na salt (comparative example)	3/97	89/11	46 ⁶	40 ⁶
p-Toluene sulfonic acid (comparative example)			33	12
Dodecylbenzene sulfonic acid ⁵ (comparative example)			30 ⁶	28 ⁶
Tide alone (comparative example)			24 ⁸	11 ⁸

1. DAMS DPO = Dialkylated monosulfonated diphenyl oxide.
2. DA BSA = Dialkylated benzene sulfonic acid.
3. Aristol E, Pilot Chemical.
4. MAMS DPO = Monoalkylated monosulfonated diphenyl oxide.
5. BIO SOFT S-100[®], Stepan.
6. Average of 2 tests.
7. Contains 3% trialkylated or higher alkylates
8. Average of 20 tests.
cleaning obtained. However, with the C₁₈ alkyl chain

-37-

length superior performance is observed with diphenyl oxide than with the MAMS toluene aromatic moiety.

Table 6

The Influence of Type of Aromatic Moiety on Cleaning Performance

Sulfonated Surfactant ¹	Percent Clean	
	Cotton	Polyester/cotton
C ₂₀₋₂₄ MAMS Diphenyl oxide	75 ⁶	46 ⁶
C ₂₀₋₂₄ MAMS Biphenyl	78 ⁷	50 ⁷
C ₂₀₋₂₄ MAMS Toluene ²	77 ⁶	47 ⁶
..... C ₂₀₋₂₄ MAMS Benzene ³	75	57
..... C ₂₀₋₂₄ MAMS Benzene ⁴	77	52
..... C ₁₈ MAMS Diphenyl oxide	60 ⁶	40 ⁶
..... C ₁₈ MAMS Toluene ⁵	42	31

1. MAMS - monoalkylated monosulfonated
2. Aristol F, Pilot Chemical.
3. Aristol A alkylate, Pilot Chemical, sulfonated with one mole of chlorosulfonic acid per mole of alkylate.
4. Aristol A alkylate, Pilot Chemical, sulfonated with one mole of sulfur trioxide per mole of alkylate.
5. Aristol G, Pilot Chemical.
6. Average of 6 tests.
7. Average of 2 tests.

B. Ratio of Sulfonated Alkylated Aromatic Surfactant to Nonionic Surfactant

The influence of the ratio of the sulfonated alkylated aromatic surfactant to nonionic surfactant is illustrated in Figure 3 for a MAMS diphenyl oxide which is 74.2 weight percent monoalkylated of C₂₀₋₂₄ and 86 percent monosulfonation. The results in Figure 3 clearly show that there is a synergistic cleaning performance obtained with the mixed surfactant system.

-38-

The optimum performance is obtained with a weight ratio of about 1 part of the sulfonated alkylated aromatic surfactant to 3 parts of the nonionic surfactant.

C. Influence of Ionization of the Sulfonic Acid

5

The anionic surfactants in salt form are preferably used in cleaning formulations for cleaning stains such as blood. Cleaning formulations of the present invention are prepared using 1 part by weight
10 monosulfonated monoalkylated aromatic surfactant to 3 parts by weight Igepal CO-520 in which the sulfonic acid is neutralized with various bases. The monosulfonated monoalkylated aromatic surfactant consists of either
15 C₂₀₋₂₄ MAMS toluene (Aristol F sulfonic acid, Pilot Chemical) or C₂₀₋₂₄ MAMS DPO (with a mono-/disulfonation ratio of 86/14 and a mono/ dialkylation ratio of 74.2/25.8). Each formulation contains 10 weight percent
20 water based on the total formulation weight. The data is summarized in Figure 4 and Table 7. The data demonstrates that neutralization of the sulfonated alkyl aromatics in a cleaning composition results in a similar cleaning performance to the unneutralized form.

25

D. Addition of Water

The influence of water on cleaning performance is illustrated in Figures 5 and 6 for formulations containing Igepal CO-520 nonionic surfactant. Two
30 different types of alkyl aromatic surfactants are used: In Figure 5 the data were obtained for a formulation with 1 part by weight of a MAMS diphenyl oxide with a mono/disulfonation ratio of 86/14 and a mono/dialkylation ratio of 74.2/25.8 for 3 parts by weight of Igepal CO-520. In Figure 6, 1 part by weight

-39-

Table 7

<u>Counterion</u>	<u>MAMS DPO %Clean Cotton</u>	<u>MAMS DPO %Clean PEC</u>	<u>MAMS Toluene %Clean</u>	<u>MAMS Toluene %Clean</u>
1 H	78	50	76	51
2 Na	66	49	75	53
3 NH ₄	74	59	66	55
4 Ca/2	77	41	55	42
5 DEA	69	45	72	57
6 TEA	67	46	70	55

of C20-24 monoalkylated toluene sulfonic acid (Aristol
F, Pilot Chemical) was used for 3 parts by weight of
15 Igepal CO-520.

Both Figure 5 and 6 show that cleaning better
than that obtained with TIDE alone (Table 4) can be
obtained with water levels of up to 80 wt% in the
20 formulations. These figures also show that a small
amount (about 10%) of water may be beneficial.

25

30

E. Type and HLB of Nonionic Surfactant

5 The influence of the type and HLB of the nonionic
surfactant is demonstrated in Tables 8 and 9. These
Tables present the data on the cleaning of cotton
swatches in Table 8 and that of polyester/cotton
10 swatches in Table 9. The pretreatment formulations
contain 1 part by weight of sulfonated alkylated
aromatic surfactant per 3 parts by weight nonionic
surfactant. The data demonstrate that cleaning
15 performance is enhanced by the cleaning compositions
comprised of the sulfonated alkylated aromatic
surfactants of this invention in combination with either
a nonylphenol ethoxylate (Tergitol or Igepal) or a
linear alcohol ethoxylate (Neodol) over the HLB range of
8.9 to 13.0.

20

25

30

- 41 -

Table 8: The Influence of HLB of the Nonionic Surfactant Included with the Sulfonated Akiyate Aromatic Surfactant on the Percent Clean for Cotton (Nonionic Surfactant/Sulfonated Akiyate Aromatic Surfactant= 3/1 [w/w])

Nonionic Surfactant	HLB	None	Percent Clean for Cotton Fabric with SAA Surfactant			
			BIO SOFT S-100®	C18 MAMS Toluene1	C20-24 MAMS DPO	C20-24 MAMS Toluene2
Tergitol NP-4	8.9	23	40	86	84	84
Igepal CO-520	10.0	12	26	42	80	81
Tergitol NP-6	10.9	21	30	46	-	-
Tergitol NP-7	11.7	19	-	-	52	72
Igepal CO-630	13.0	15	20	26	-	-
Neodol Blend 1	9.0	28	29	55	52	73
Neodol Blend 2	10.0	33	25	39	-	-
Neodol Blend 3	11.4	36	27	37	-	-
Neodol 23-5	10.7	21	25	34	52	65
Neodol 45-7	11.8	39	31	46	52	77
Neodol 25-9	13.1	25	26	50	-	-

1. Aristol G sulfonic acid, Pilot Chemical Company.
2. Aristol F sulfonic acid, Pilot Chemical Company.

Table 9: The Influence of HLB of the Nonionic Surfactant Included with the Sulfonated Akylated Aromatic Surfactant on the Percent Clean for Polyester/Cotton Blend (Nonionic Surfactant/Sulfonated Akylate Aromatic Surfactant=3/1 [w/w])

Nonionic Surfactant	HLB	None	Percent Clean for Cotton Fabric with SAA Surfactant			
			BIO SOFT S-100®	C18 MAMS Toluene1	C20-24 MAMS DPO	C20-24 MAMS Toluene2
Tergitol NP-4	8.9	8	10	35	33	33
Igepal CO-520	10.0	16	28	31	54	48
Tergitol NP-6	10.9	22	26	31	-	-
Tergitol NP-7	11.7	11	-	-	39	56
Igepal CO-630	13.0	13	20	30	-	-
Neodol Blend 1	9.0	11	13	24	27	38
Neodol Blend 2	10.0	17	16	21	-	-
Neodol Blend 3	11.4	29	20	34	-	-
Neodol 23-5	10.7	12	13	22	27	39
Neodol 45-7	11.8	26	19	30	37	56
Neodol 25-9	13.1	20	14	32	-	-

1. Aristol G sulfonic acid, Pilot Chemical Company.
2. Aristol F sulfonic acid, Pilot Chemical Company.

-43-

E. Stick Formulation

A stick formulation is prepared with the following composition:

5	Norpar 15	40 g
	Neodol 45-7	12 g
	Igepal CO-520	12 g
	PEG E-900 (Dow) ¹	2 g
10	Na ₂ CO ₃	2 g
	DI Water	6 g
	Aristol F (or for DBSA this is BIOSOFT S-100®)	5 g
15	Stearic Acid	2 g
	Cottonseed Oil	10 g
	Enzyme (Proteolytic)	2 g
	Total	93 g
20	1. Polyglycol E900 (Dow) polyethylene glycol	
25		
30		

-44-

The comparisons in Tables 10 illustrate that similar cleaning performance is obtained with compositions of this invention using a stick (solid) as well as liquid cleaning formulations.

5

Table 10

CLEANING PERFORMANCE
OF STICK FORMULATIONS
SAMPLES

10

SAMPLE IDENTIFICATION	PERCENT COTTON	CLEAN POLYESTER/ COTTON
Aristol "F" Stick	74	51
DDBSA Stick	40	29
Tide only no Pretreatment	28	11

20

25

30

Experimental

Stick hardness is measured in accordance with ASTM standard D-127. The procedure uses an ASTM penetrometer equipped with a standard cone (150 g) without additional weight added. Stick hardness is reflected by the depth the cone penetrates into the stick in five seconds. The depth is reported in 0.1 mm. Thus a higher number describes a softer stick. Each stick in this example has a stick hardness of 92.

10

15

20

25

30

WHAT IS CLAIMED IS:

1. A cleaning composition, comprising:
 - a) a nonionic surfactant; and
 - b) a sulfonated alkylated aromatic surfactant, said sulfonated alkylated aromatic surfactant containing an aromatic moiety having 1 to 3 benzene rings and having at least one sulfonate group, provided that when the aromatic moiety contains more than one benzene ring, disulfonate is present in less than about 50 percent of the total sulfonated alkylated aromatic surfactant, said sulfonated alkylated aromatic surfactant having at least one alkyl group of from C₁₈ up to about C₃₀;wherein the weight ratio of sulfonated alkylated aromatic surfactant to nonionic surfactant is about 1:19 to about 3:2.

2. The cleaning composition of Claim 1, wherein the aromatic moiety is benzene, toluene, xylene, naphthalene, diphenyl oxide, biphenyl, or biphenylphenyl ether.

3. The cleaning composition of Claim 1, wherein said nonionic surfactant has a hydrophilic

-47-

lipophilic balance (HLB) value in the range of from about 8 to about 15.

4. The cleaning composition of Claim 1,
wherein said nonionic surfactant has a hydrophilic
lipophilic balance (HLB) value in the range of from
5 about 8 to about 13.

5. The cleaning composition of Claim 1,
wherein said nonionic surfactant has a hydrophilic
lipophilic balance (HLB) value in the range of from
10 about 9 to about 13.

6. The cleaning composition of Claim 1,
wherein the weight ratio of said sulfonated alkylated
aromatic surfactant to said nonionic surfactant is from
15 about 1:9 to about 1:1.

7. The cleaning composition of Claim 1,
wherein the weight ratio of said sulfonated alkylated
aromatic surfactant to said nonionic surfactant is from
20 about 1.5:8.5 to about 3:7.

8. The cleaning composition of Claim 1,
further comprising water in an amount below about 80
weight percent of the total cleaning composition.
25

9. The cleaning composition of Claim 1,
further comprising water in an amount below about 30
weight percent of the total cleaning composition.

30 10. The cleaning composition of Claim 1,
further comprising water in an amount from about 5 to
about 20 weight percent of the total cleaning
composition.

-48-

11. A cleaning composition, comprising:
a) a nonionic surfactant; and
b) a sulfonated alkylated aromatic
surfactant, said sulfonated alkylated aromatic
surfactant containing an aromatic moiety having 1 to 3
benzene rings and having at least one sulfonate group,
5 provided that when the aromatic moiety consists of more
than one benzene ring, disulfonate is present in less
than about 50 percent of the total sulfonated alkylated
aromatic surfactant, said sulfonated alkylated aromatic
10 surfactant having at least one alkyl group of from C₁₈
up to about C₃₀;
wherein the cleaning composition is in the form of a
solid stick.
- 15 12. The cleaning composition of Claim 11,
wherein the solid-stick form is obtained by further
comprising the cleaning composition of a sufficient
amount of stearic acid and neutralent for the stearic
acid.
- 20 13. The cleaning composition of Claim 11,
wherein the weight ratio of said sulfonated alkylated
aromatic surfactant to said nonionic surfactant is about
1:19 to about 3:2.
- 25 14. The cleaning composition of Claim 11,
further comprising water in an amount below about 30
weight percent of the total cleaning composition.
- 30 15. The cleaning composition of Claim 11,
further comprising water in an amount from about 5 to
about 20 weight percent of the total cleaning
composition.

-49-

16. A method of cleaning a soil from a surface or fabric, comprising the step of: contacting the soil with a cleaning composition comprising:

- a) a nonionic surfactant;
- b) a sulfonated alkylated aromatic
5 surfactant, said sulfonated alkylated aromatic surfactant containing an aromatic moiety having 1 to 3 benzene rings and having at least one sulfonate group, provided that when the aromatic moiety consists of more than one benzene ring, disulfonate is present in less
10 than about 50 percent of the total sulfonated alkylated aromatic surfactant, said sulfonated alkylated aromatic surfactant having at least one alkyl group of from C₁₈ up to about C₃₀; and
- c) water in amount below about 80 weight
15 percent of the total cleaning composition.

17. The method of Claim 16, wherein said water is present in an amount below about 30 weight percent of the total cleaning composition.
20

18. The method of Claim 16, wherein said water is present in an amount from about 5 to about 20 weight percent of the total cleaning composition.

25 19. A method of cleaning a soil from a surface or fabric, comprising the step of: contacting the soil with the cleaning composition comprising:

- a) a nonionic surfactant; and
- b) a sulfonated alkylated aromatic
30 surfactant, said sulfonated alkylated aromatic surfactant containing an aromatic moiety having 1 to 3 benzene rings and having at least one sulfonate group, provided that when the aromatic moiety contains more than one benzene ring, disulfonate is present in less

-50-

than about 50 percent of the total sulfonated alkylated aromatic surfactant, said sulfonated alkylated aromatic surfactant having at least one alkyl group of from C₁₈ up to about C₃₀;
wherein the weight ratio of sulfonated alkylated aromatic surfactant to nonionic surfactant is about 1:19 to about 3:2.

20. A method of cleaning a soil from a surface or fabric, comprising the step of: contacting the soil with the cleaning composition comprising:

- a) a nonionic surfactant; and
- b) a sulfonated alkylated aromatic surfactant, said sulfonated alkylated aromatic surfactant containing an aromatic moiety having 1 to 3 benzene rings and having at least one sulfonate group, provided that when the aromatic moiety consists of more than one benzene ring, disulfonate is present in less than about 50 percent of the total sulfonated alkylated aromatic surfactant, said sulfonated alkylated aromatic surfactant having at least one alkyl group of from C₁₈ up to about C₃₀;

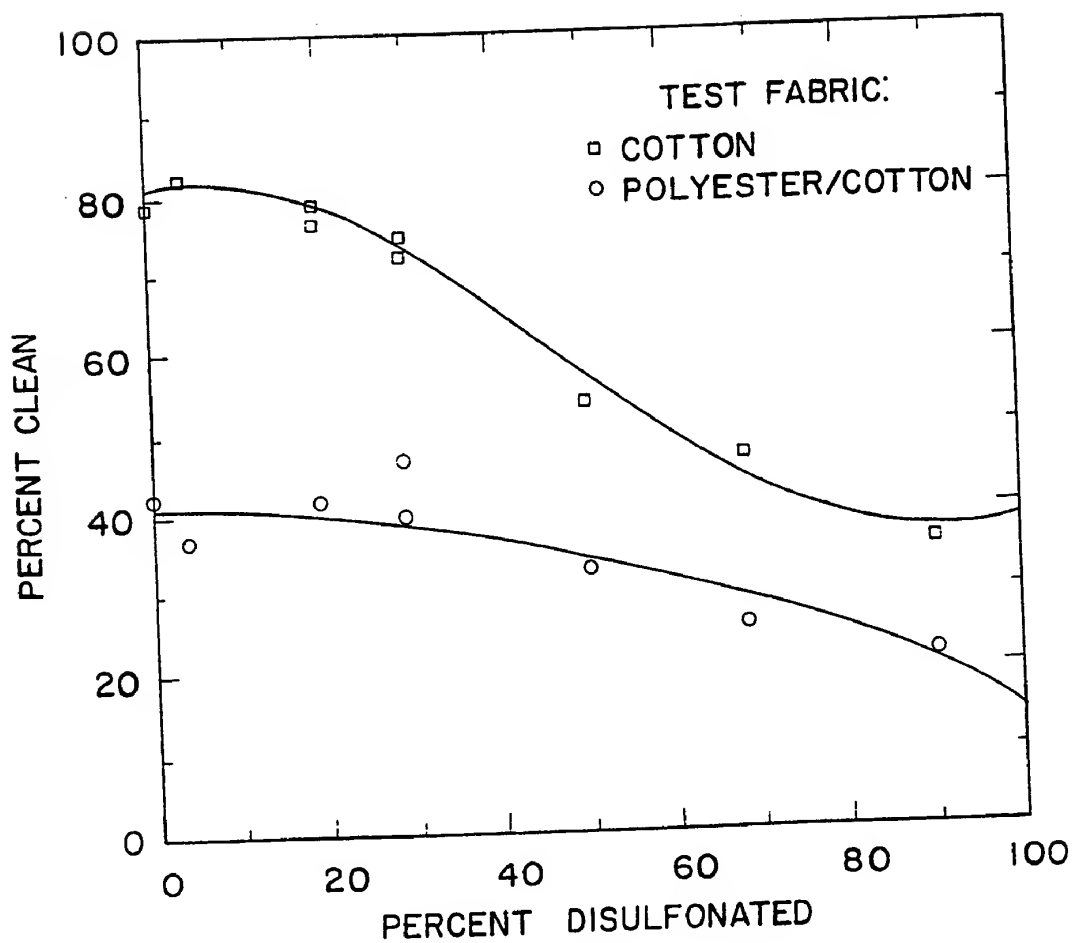
wherein the cleaning composition is in the form of a solid stick.

25

30

1 / 6

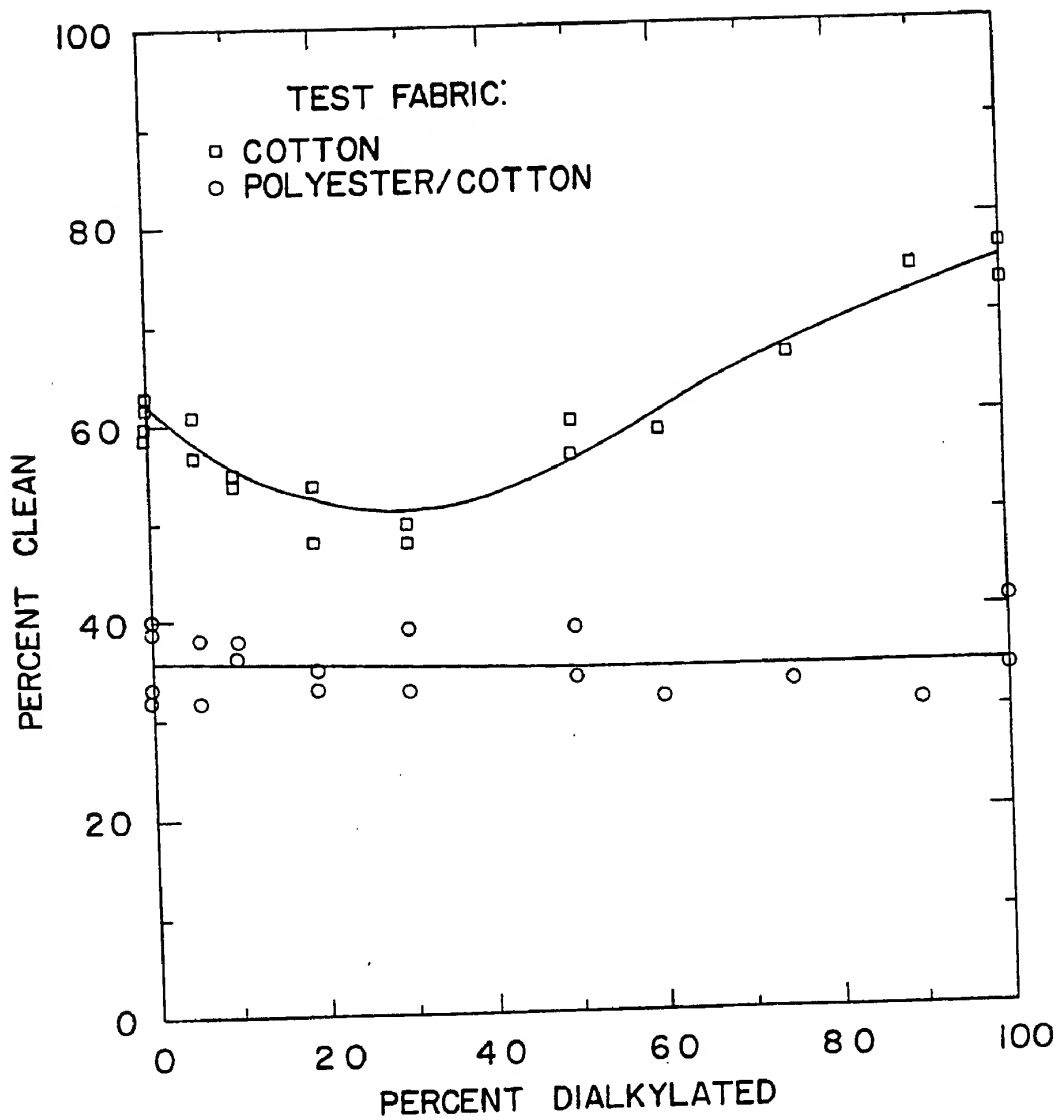
FIG. 1



SUBSTITUTE SHEET

2 / 6

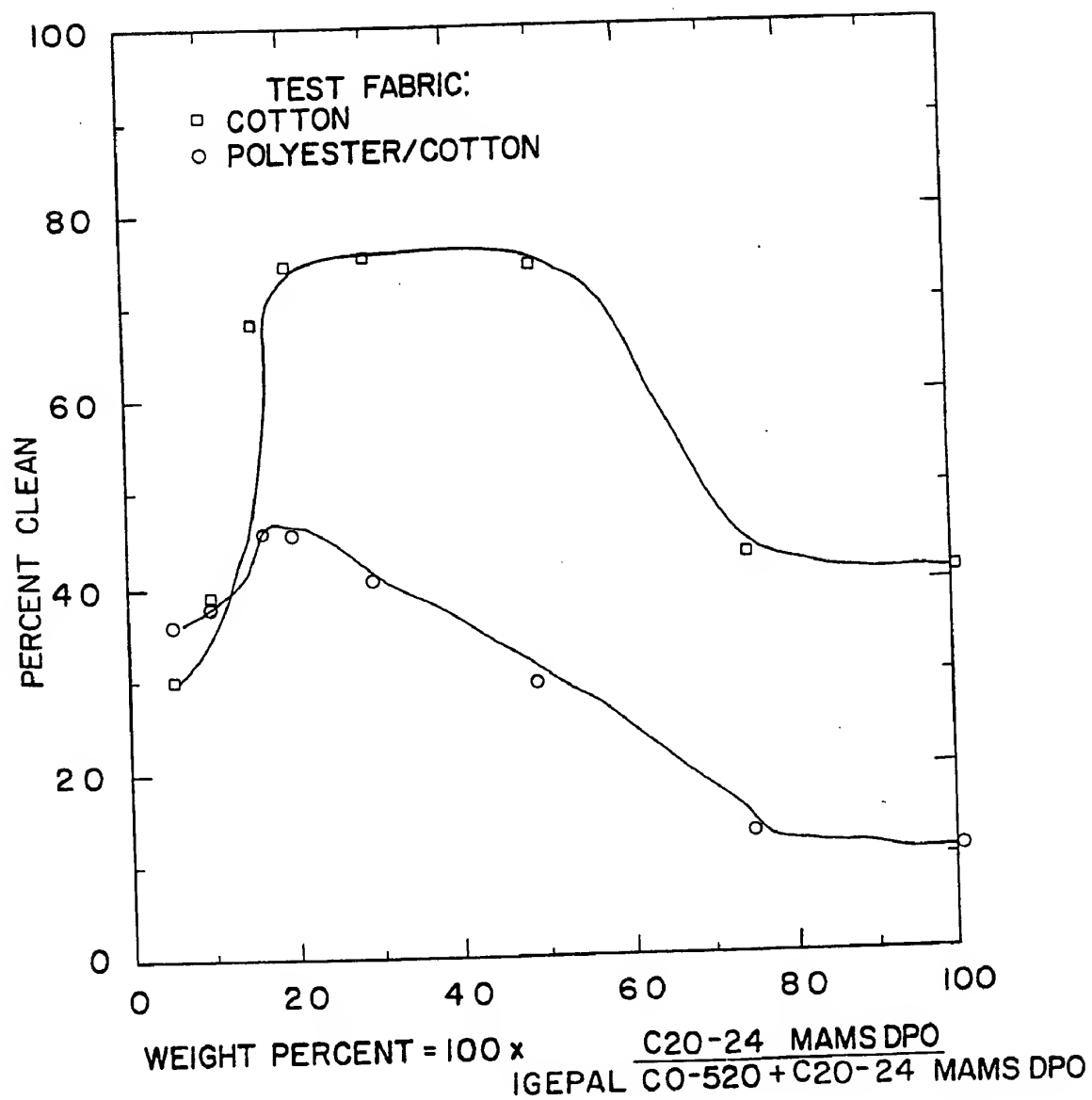
FIG. 2



SUBSTITUTE SHEET

3/6

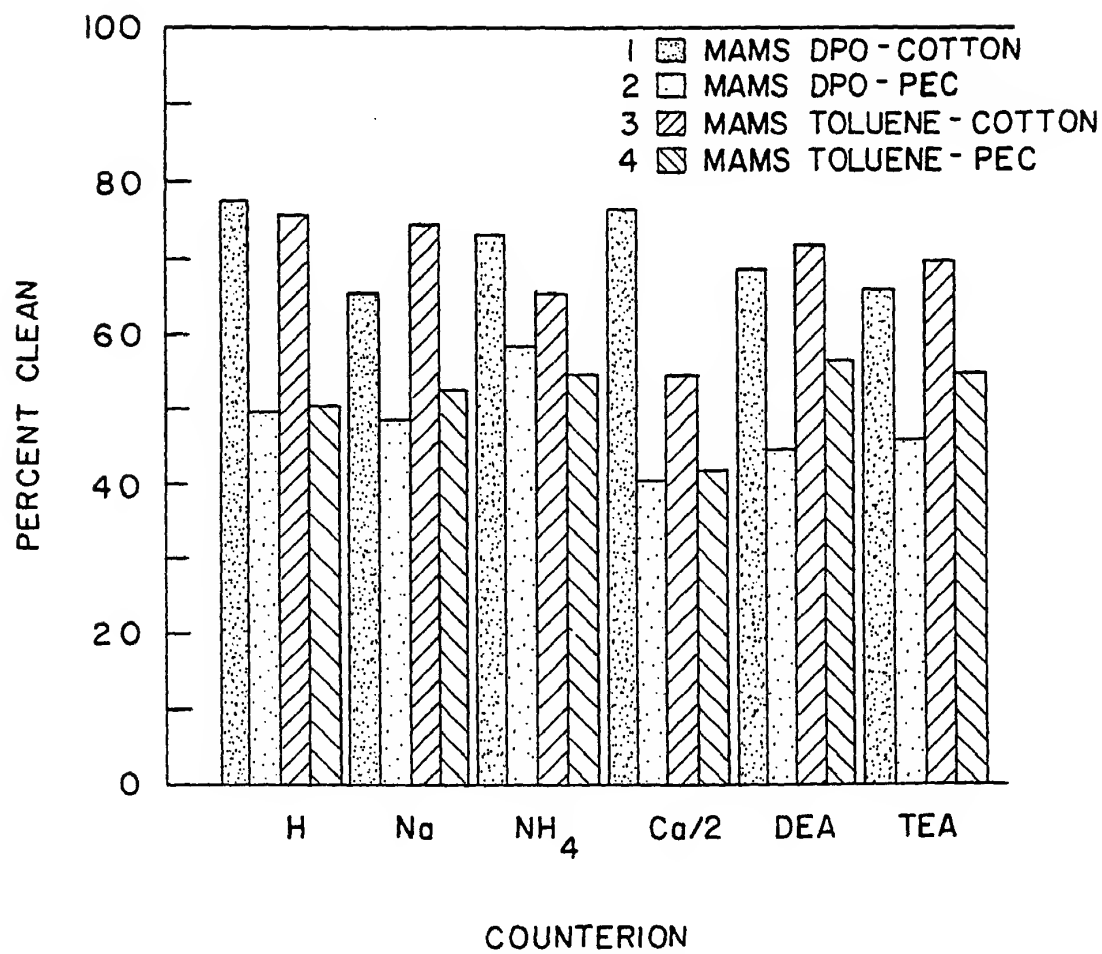
FIG. 3



SUBSTITUTE SHEET

4 / 6

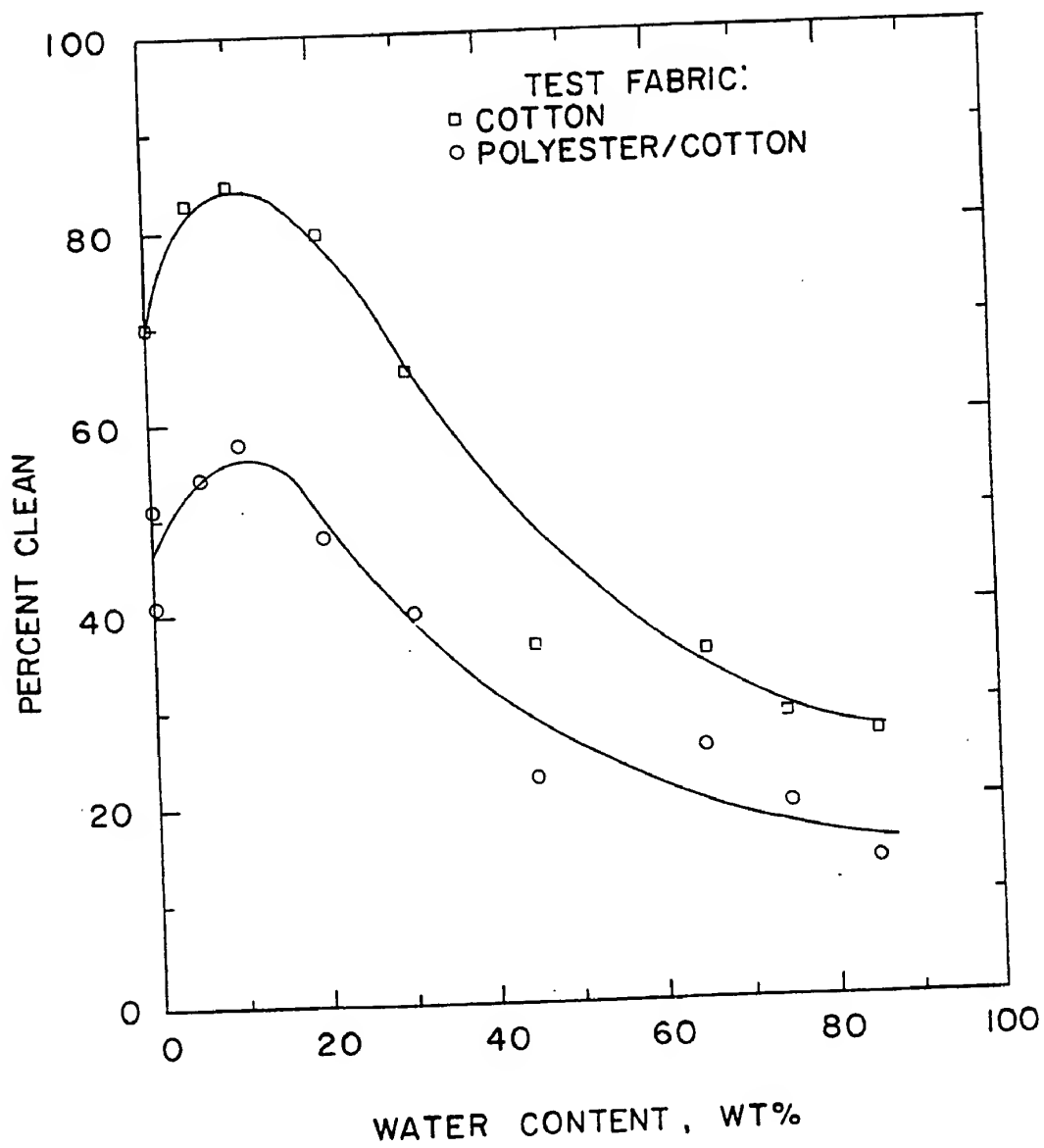
FIG. 4



SUBSTITUTE SHEET

5 / 6

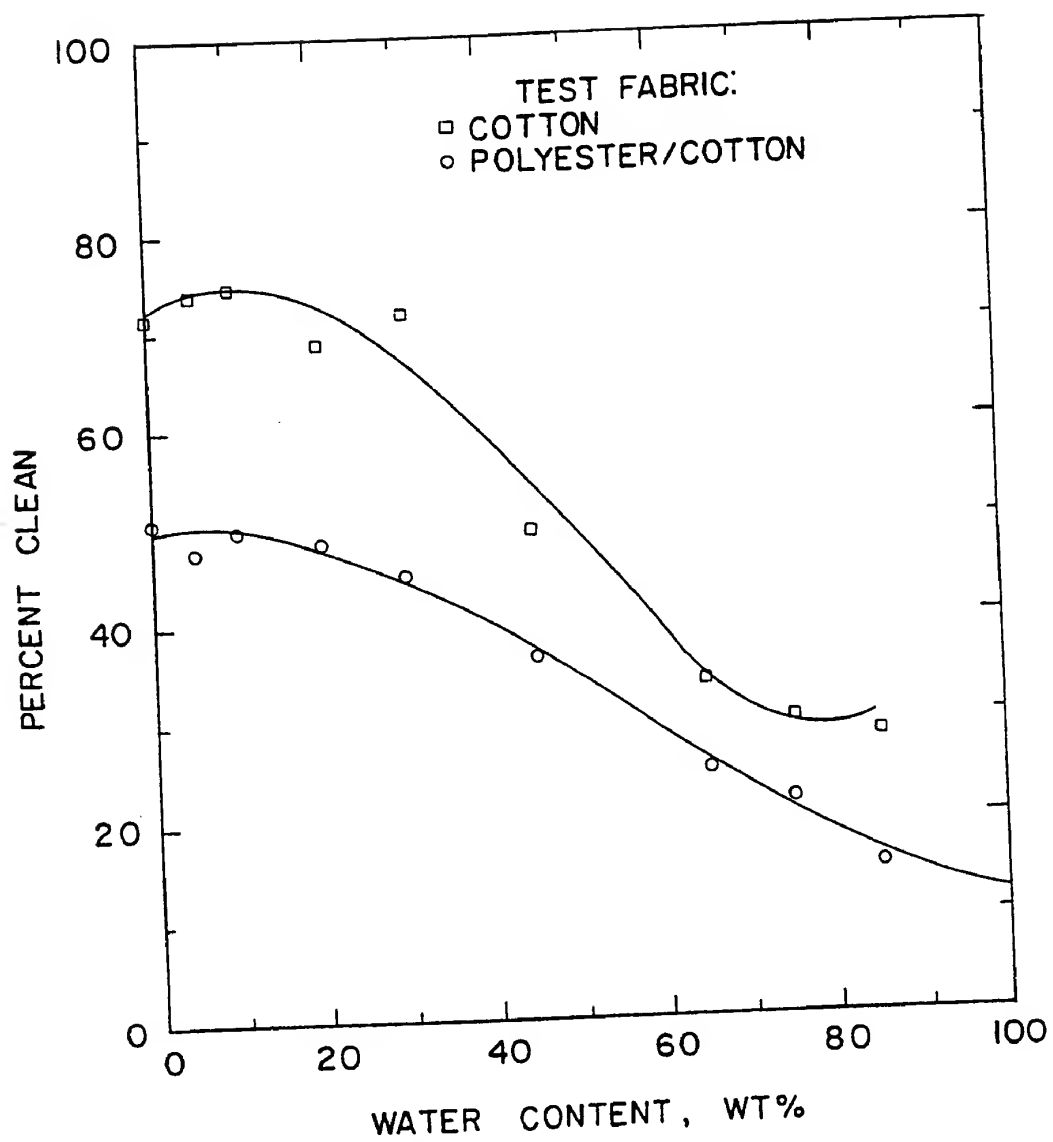
FIG. 5



SUBSTITUTE SHEET

6/6

FIG. 6



SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/08080

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C11D 1/83 3/34; 1/831;

US CL : 252/559; 252/134;

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/559; 134; 174; DIG 19; 558

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS (automated patent system): Sulfate#, Sulphom?, Sulfonate#,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,880,778 (House) 29 April 1975. Entire Document.	1-20
Y	US, A, 4,347,168 (Murphy et al) 31 August 1982. Entire Document.	1-20
Y	US, A, 4,123,395 (Maguire Jr. et al) 31 October 1978. Entire Document.	1-20
Y	US, A, 4,088,598 (Williams) 09 May 1978. Entire Document.	1-20
Y	US, A, 4,683,008 (Betts) 28 July 1987. Entire Document.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:		*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A	document defining the general state of the art which is not considered to be part of particular relevance	*X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E	earlier document published on or after the international filing date	*Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z	document member of the same patent family
*O	document referring to an oral disclosure, use, exhibition or other means		
*P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

10 OCTOBER 1993

Date of mailing of the international search report

28 DEC 1993

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

PAUL LIEBERMAN

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/08080

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,842,762 (Sabol, Jr. et al) 27 June 1989. Entire Document.	1-20